

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-279474

(43)Date of publication of application : 12.10.1999

(51)Int.CI.
 C09D 11/10
 B41J 2/01
 C09K 11/06
 C09K 11/06

(21)Application number : 11-015049

(71)Applicant : MITSUI CHEM INC

(22)Date of filing : 25.01.1999

(72)Inventor : SHIMAMURA TAKEHIKO
NAKATSUKA MASAKATSU
TAKUMA HIROSUKE

(30)Priority

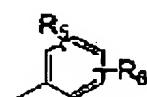
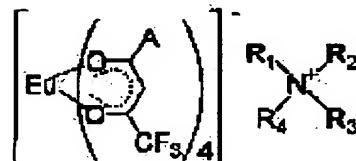
Priority number : 10 14341 Priority date : 27.01.1998 Priority country : JP

(54) INK COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an ink composition with high storage stability capable of affording printed matter which is colorless under ordinary visible light but radiates red when irradiated with ultraviolet rays, by including an arylsulfonic acid and a tertiary amine.

SOLUTION: This ink composition contains a fluorescent compound of formula I [A is a group of formula II (R5 and R6 are each H, a halogen, alkyl or the like) or the like; R1 to R4 are each H, an alkyl or aralkyl], an arylsulfonic acid (e.g. benzenesulfonic acid) and a tertiary amine (e.g. triethylamine); wherein it is preferable that this composition also contains, as binder resin, at least one kind selected from polyvinylpyrrolidone, ethyl cellulose and polyvinyl butyral, and ethanol account for ≥ 70 wt.% of the whole composition.



LEGAL STATUS

[Date of request for examination] 22.07.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

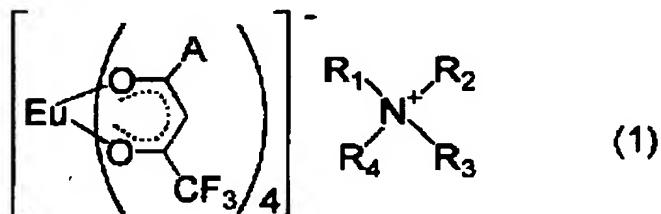
*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

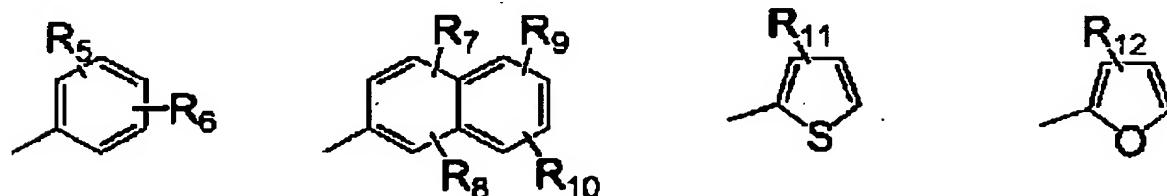
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

[Claim(s)]

[Claim 1] An ink constituent characterized by containing aryl sulfonic acids and tertiary amine in an ink constituent containing a fluorescence compound expressed with the following general formula (1) and (** 1).

[Formula 1]

The inside of [type and A] are either of the substituents expressed with the following type (** 2). [Formula 2]



It means (R5 -R12 express a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, the amino group, an alkylamino radical, a dialkylamino radical, an aryl group, or an aralkyl radical independently among a top type, respectively), and is R1 -R4.] which may show a hydrogen atom, an alkyl group, or an aralkyl radical, may join together mutually, and may make annular independently, respectively

[Claim 2] An ink constituent according to claim 1 whose 70 % of the weight or more is ethanol to weight of the whole ink constituent including at least one sort of a polyvinyl pyrrolidone, ethyl cellulose, and a polyvinyl butyral as binder resin.

[Detailed Description of the Invention]**[0001]**

[The technical field to which invention belongs] This invention is colorlessness under the usual light, and relates to the ink constituent containing the fluorescence compound which colors in red under the exposure of ultraviolet rays.

[0002]

[Description of the Prior Art] For the purpose, such as a nondisclosure and forged prevention, etc., in the usual light, it is hard to carry out a check, and it visualizes with ultraviolet rays or infrared radiation, or development of the ink which makes reading by the sensor possible is performed. As a fluorescence compound used for such ink, since a Stokes shift is large and luminescence reinforcement is also large, rare earth complexes, such as tetrabutylammonium tetrakis [4, 4, 4-trifluoro-1-(2-thienyl)-1, and 3-butane dionate] europium, can prevent a reading mistake, and are suitable compounds. For example, the fluorescence ink constituent of the colorlessness or light color which uses a rare earth complex as a fluorescence compound component is proposed as an object for ink jet printing (JP,54-22336,B, JP,08-239607,A, JP,09-188835,A).

[0003] Ink jet printing injects ink from a nozzle, and since it is a method made to adhere to a recorded object, also to the surface which this nozzle and a recorded object do not touch and has a curved surface and irregularity, good printing is possible for it and it is excellent as the marking method of various information. Also in it, especially ink jet printing of a continuous method electrifies the injected ink particle according to an electric alphabetic signal, and especially when it deflects the track of an ink drop according to the amount of electrifications, and it is the method in which an alphabetic character etc. is made to form, it excels in high-speed printing and it carries out marking of the information according to individual (for example, serial number etc.) to a lot of recorded objects with a deflecting electrode, it can be called method for which were suitable.

[0004] However, in the condition that the fluorescence intensity tends to fall and other electrolytes coexist especially gradually by dissociation of a ligand etc. in ink, such as ink for ink jet printing, the orientation of a rare earth complex is remarkable. Therefore, improvement in the conservation stability of the ink containing a rare earth complex was called for. Especially, in ink jet printing of a continuous method, since it was necessary to give conductivity to ink, the electrolyte was added as a conductive grant agent and difficulty usually followed on use of a rare earth complex. Although the above-mentioned patent application had the feature in a fluorochrome and binder resin, respectively, also when using it for a continuous method, it was using compounds usually known for the time being in the fields, such as lithium salt and quarternary

ammonium salt, as a conductive grant agent, and was not able to say the conservation stability of ink with it being enough.

[0005]

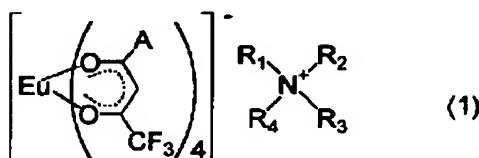
[Problem(s) to be Solved by the Invention] Under the usual light, the technical problem of this invention is colorlessness and is to offer the ink constituent which the record object which emits light in red was obtained when ultraviolet rays were irradiated, and was excellent in the conservation stability of ink.

[0006]

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of examining the above-mentioned technical problem wholeheartedly. That is, this invention relates to an ink constituent of the aforementioned ** whose 70 % of the weight or more is ethanol to weight of the whole ink constituent including at least one sort of a polyvinyl pyrrolidone, ethyl cellulose, and a polyvinyl butyral in an ink constituent containing a fluorescence compound expressed with the ** following general formula (1) and (** 3) as an ink constituent characterized by containing aryl sulfonic acids and tertiary amine, and ** binder resin.

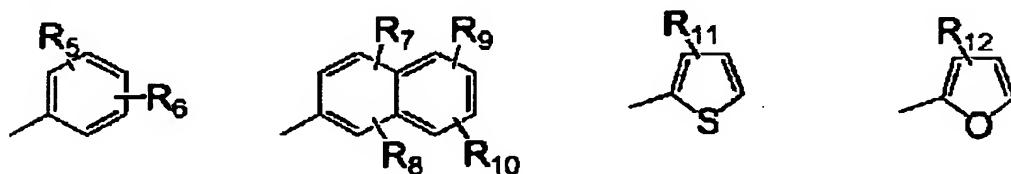
[0007]

[Formula 3]



The inside of [type and A are either of the substituents expressed with the following type (** 4). [0008]

[Formula 4]



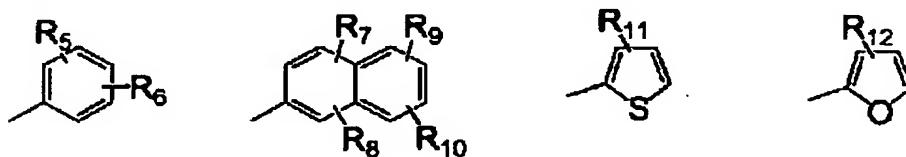
It means (R5 -R12 express a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, the amino group, an alkylamino radical, a dialkylamino radical, an aryl group, or an aralkyl radical independently among a top type, respectively), and is R1 -R4.] which may show a hydrogen atom, an alkyl group, or an aralkyl radical, may join together mutually, and may make annular independently, respectively

[0009]

[Embodiment of the Invention] Hereafter, this invention is explained to details. This invention is an ink constituent characterized by containing aryl sulfonic acids and tertiary amine in the ink constituent containing the fluorescence compound expressed with said general formula (1). The fluorescence compound (it is also called a fluorescence material) used with the ink constituent of this invention is an europium complex expressed with said general formula (1). R1 -R4 in a general formula (1) Independently, a hydrogen atom, an alkyl group, or an aralkyl radical may be shown, it may connect mutually, and you may make annular, respectively. As the concrete example, a hydrogen atom, alkyl groups (for example, a methyl group, an ethyl group, butyl, an octyl radical, etc.), and aralkyl radicals (for example, benzyl, a phenethyl radical, etc.) can be mentioned. Moreover, R1 -R4 As an example which connects mutually and makes annular, N-MECHIRUPI ** RIJINIUMU, N-BENJIRUPI ** RIJINIUMU, N, and N-dimethyl PIROJINIUMU, N, and N-diethyl PIROJINIUMU etc. is mentioned, for example. Moreover, A expresses either of the substituents which is expressed with the following type (** 5).

[0010]

[Formula 5]



(R5 -R12 express the same semantics as the above among a top type)

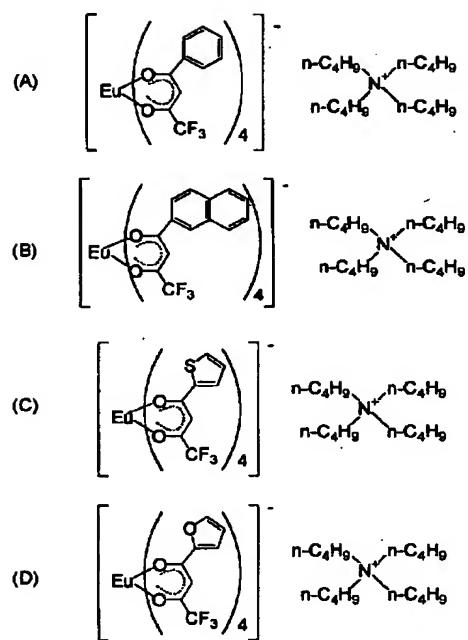
[0011] In the above-mentioned substituent as a concrete example of R5 -R12 A hydrogen atom, a halogen atom (for example, a fluorine atom, a chlorine atom, a bromine atom, etc.), An alkyl group (for example, a methyl group, an ethyl group, an isopropyl group, etc.), An alkoxy group (for example, a methoxy group, an ethoxy radical, a butoxy radical, etc.), The amino group, an alkylamino radical (for example, a methylamino radical, an ethylamino radical, etc.), Dialkylamino radicals (for example, a dimethylamino radical, a diethylamino radical, etc.), aryl groups (for example, a phenyl group, p-tolyl group, etc.), and aralkyl radicals (for example, benzyl, a phenethyl radical, etc.) can be mentioned.

[0012] As an example of an europium complex expressed with the general formula (1) used by this invention, although the instantiation compound expressed with following formula (A) - (X) and (** 6-11) can be mentioned, this invention is not limited to these instantiation compounds, for example.

[0013]

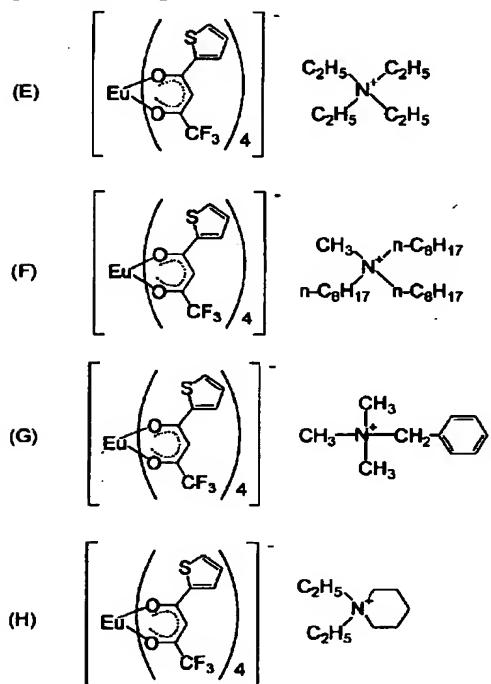
[Formula 6]

例示化合物



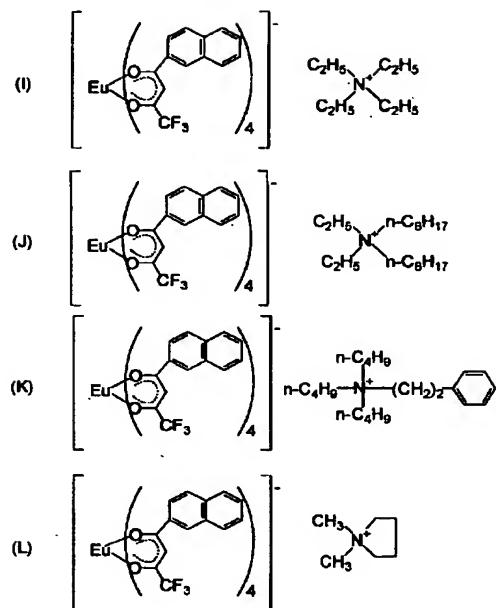
[0014]

[Formula 7]



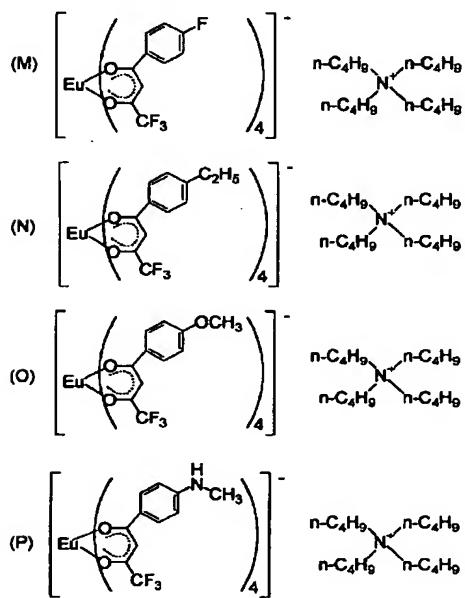
[0015]

[Formula 8]



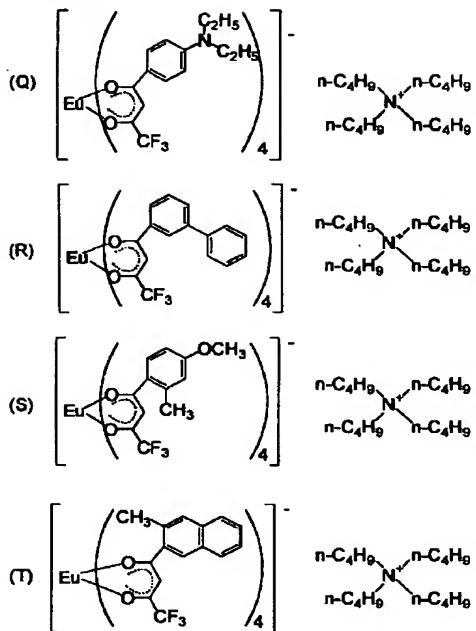
[0016]

[Formula 9]



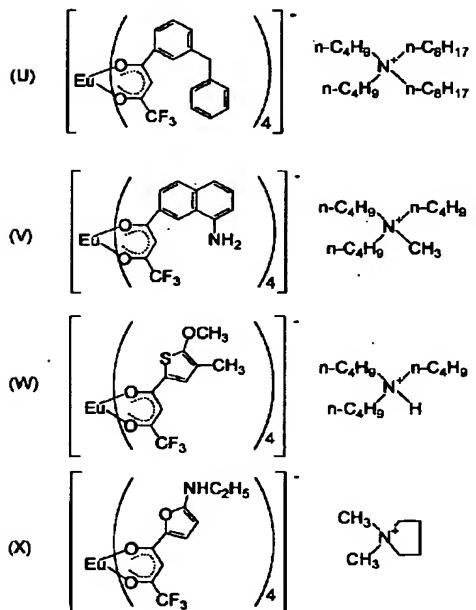
[0017]

[Formula 10]



[0018]

[Formula 11]

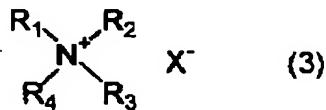
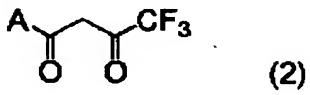


[0019] The europium complex expressed with the general formula (1) used by this invention is compoundable according to the method of a publication to JP,64-6085,A, JP,64-26583,A, etc. For example, it is easily compounded by reacting perchloric acid

euroium and the compound of the following general formula (2) and (** 12) under sodium-hydroxide existence and in an acetone, and subsequently making the ammonium salt of a general formula (3) and (** 12) act on the obtained compound.

[0020]

[Formula 12]



(Among a top type, X expresses a halogen atom and A and R1 -R4 express the same semantics as the above.)

[0021] The aryl sulfonic acids used in the ink constituent of this invention are the aromatic compounds which are replaced by one or more sulfonic groups and may have other substituents. As a concrete example of aryl sulfonic acids For example, benzenesulfonic acid, p-chlorobenzene sulfonic acid, p-phenolsulfonic acid, o-toluenesulfonic acid, p-toluenesulfonic acid, a sulfanilic acid, p-ethylbenzene sulfonic acid, alpha-naphthalene sulfonic acid, beta-naphthalene sulfonic acid, A 2-naphthol-8-sulfonic acid, the 1-naphthol -3, 6-disulfonic acid, 2-naphthol-3, 6-disulfonic acid, 1-amino-8-hydroxy naphthalene -3, 6-disulfonic acid, 4-biphenyl sulfonic acid, 9, 10-dimethoxyanthracene sulfonic acid, an anthraquinone-2-sulfonic acid, anthraquinone -2, 6-disulfonic acid, etc. are mentioned. These parts are marketed and are easily available. Preferably, it is the naphthalene sulfonic acid which is not replaced [the benzenesulfonic acid which is not replaced / substitute or /, substitute, or].

[0022] Moreover, the tertiary amine used in the ink constituent of this invention is the compounds with which all three of the hydrogen atoms of ammonia were independently replaced by the alkyl group, the hydroxyalkyl radical, or the aralkyl radical, respectively. As the concrete example, triethylamine, tree n propylamine, tree n butylamine, dimethylethanamine, diethyl ethanamine, triethanolamine, N, and N-dimethyl benzylamine, N, and N-diethyl benzylamine, N, and N-dimethyl phenethylamine etc. is mentioned, for example. These parts are marketed and are easily available.

[0023] The ink constituent of this invention is a constituent containing the fluorescence compound and aryl sulfonic acids which are expressed with said general formula (1), tertiary amine, and a solvent, further, may contain the binder and may contain other various additives if needed. In the ink constituent of this invention, the concentration of a fluorescence compound is 0.01 - 1 % of the weight more preferably 0.001 to 10% of the weight as concentration in an ink constituent that what is necessary is just in the limit dissolved in the solvent to be used or a binder. The concentration of the aryl sulfonic

acids in an ink constituent is 0.1 - 2 % of the weight preferably 0.01 to 5% of the weight. Moreover, tertiary amine is 0.1 - 2 % of the weight preferably 0.01 to 10% of the weight among an ink constituent. In addition, although aryl sulfonic acids and tertiary amine may use one sort of each at a time, they may be used combining several sorts.

[0024] In the ink constituent of this invention, it is required 5-10, and to keep pH of an ink constituent more desirable at 6-9. In this invention, the operating rate of aryl sulfonic acids and tertiary amine can be adjusted, and pH can be adjusted. If pH separates from this range, disassembly of a fluorescence compound becomes is easy to be promoted, and it is not desirable.

[0025] In the ink constituent of this invention, an organic solvent and/or water can be used as a solvent of ink. As an organic solvent which can be used for the ink constituent of this invention That what is necessary is just what can dissolve the fluorescence compound expressed with a general formula (1), and the binder resin used by this invention for example, a fatty alcohol system solvent (for example, a methanol and ethanol --) Propanol, ethylene glycol, a diethylene glycol, a polyethylene glycol, ketones (for example, an acetone and ethyl methyl ketone --), such as a glycerol ester solvents (for example, ethyl acetate --), such as methyl isobutyl ketone ethers solvents (for example, methyl cellosolve --), such as butyl acetate, etc. Glycol ether system solvents, such as ethylcellosolve and dioxane for example, ethylene glycol wood ether and ethylene glycol diethylether -- The diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, Glycol ester system solvents, such as the diethylene-glycol monobutyl ether for example, ethylene glycol monomethyl ether acetate and ethylene glycol monoethyl ether acetate -- N-methyl pyrrolidones, such as diethylene-glycol monomethyl ether acetate, dimethyl sulfoxide, sulfolane, 1,3-dimethyl-2-imidazolidinone, etc. are mentioned. These solvents can be used combining one sort or several sorts.

[0026] In addition, although a methyl ethyl ketone, ethyl acetate, etc. are generally used in conventional ink, on the printing business which uses the ink which makes these organic solvents a subject, there is also the necessity for work environment maintenance, such as local ventilation installation, and it is not desirable on the handling of ink. Therefore, it is desirable to make it ethanol without regulation of the subject of the organic solvent to be used of an operating environment in the ink constituent of this invention, and it is more desirable that the weight of the whole ink constituent contains ethanol 70% or more.

[0027] Moreover, in the ink constituent of this invention, various binder resin can be added according to the need for the use. The binder resin which can be used for the ink constituent of this invention fixes a fluorescence compound to a recorded object good, is

made to contain in order to prepare the viscosity of ink suitably, and if it is resin which dissolves in the organic solvent used by this invention, it will not be limited especially. For example, a polyvinyl pyrrolidone, polyurethane, polyvinyl alcohol, A polyvinyl butyral, the poly caprolactone, polyethylene glycol ester, Polystyrene, Polly alpha methyl styrene, and polyolefines For example, (polyethylene, polypropylene, etc. and ethylene-vinylacetate copolymers), Polysulfone, polyester, a polycarbonate, a styrene-acrylic-acid copolymer, polyacrylates (for example, polymethylacrylate and polyacrylic acid ethyl --) Polyacrylic acid propyl, a polymethyl methacrylate, polymethacrylic acid ethyl, The polymethyl vinyl ether, such as polymethacrylic acid propyl, a methyl-vinyl-ether-maleic-acid copolymer, A methyl-vinyl-ether-maleic-acid methyl copolymer, a methyl-vinyl-ether-maleic-acid anhydride copolymer, a cellulosic (for example, methyl cellulose and ethyl cellulose --) a propyl cellulose, hydroxyethyl cellulose, hydroxypropylcellulose, carboxymethylcellulose sodium, an acetyl cellulose, a nitrocellulose, etc. -- etc. -- it can mention.

[0028] Moreover, the resin usually used for the common ink for printing (the common version ink, letterpress ink, fluorescence ink, etc.) of natural resin and processing resin (for example, rosin, the hardened rosin, rosin ester, a shellac, etc.), synthetic resin, and its modified resin (for example, phenol resin, rosin denaturation phenol resin, a drying-oil denaturation alkyd resin, rosin denaturation maleic resin, polyamide resin, etc.), for example can also be used. Binder resin may use one kind or may use some kinds together.

[0029] In the ink constituent of this invention, in order to fill the wantage nature from which the versatility of ink differs according to terms and conditions, such as format of printing, or a class of recorded object, the presentation of a solvent and binder resin is adjusted suitably, and also further various kinds of additives can also be added. In the ink constituent of this invention, when making the subject of an organic solvent into ethanol, it is more desirable that the solubility over ethanol considers as a good polyvinyl pyrrolidone, ethyl cellulose, and a polyvinyl butyral as binder resin.

[0030] A fluorescence compound, aryl sulfonic acids, tertiary amine, a binder, and if needed, various additives etc. are added in an organic solvent and/or water, they are stirred and dissolved in the bottom of a room temperature or heating, and the ink constituent of this invention is manufactured by filtering and removing a part for an insoluble solution.

[0031] The ink constituent of this invention is an ink constituent which can be suitably used as ink for ink jet printing. Generally, as physical properties of the ink for ink jet printing, viscosity 0.8 - 15cP, and surface tension 20 - 50 dyn/cm are desirable. Furthermore, when considering as the ink for ink jet printing of a continuous method, it

is desirable to adjust specific resistance to 5000 or less ohm-cm.

[0032] When using the ink constituent of this invention as the ink for ink jet printing, as amount of the organic solvent used, it is 10 - 99.9 % of the weight to the weight of the whole ink constituent, and preferably, it is 30 - 99 % of the weight, and is 50 - 97 % of the weight still more preferably. Moreover, as for the amount of the binder resin used, it is desirable to make it not exceed 20 % of the weight to the whole weight. Since the orientation to become so high that the viscosity of ink not be suitable for ink jet printing in the content beyond this, and for desiccation of a record object to become slow is accepted, it is not desirable. The amount of the more desirable binder resin used is 0.002 - 10 % of the weight. Furthermore, various kinds of additives (for example, a desiccation inhibitor, a conductive grant agent, a surfactant, antiseptics, a rusr-proofer, metal encapsulant, etc.) can be added to the ink constituent of this invention if needed.

[0033] When using the ink constituent of this invention as the ink for ink jet printing for a continuous method, it is desirable to contain the organic solvent of a high-boiling point further for desiccation prevention of ink. As an organic solvent of the high-boiling point which suits this purpose, a water-soluble organic solvent 100 degrees C or more has the desirable boiling point, and a water-soluble organic solvent (150 degrees C or more and 250 degrees C or less) has the more desirable boiling point. As a concrete example of a high-boiling point organic solvent, for example A polyhydric-alcohol solvent for example, ethylene glycol, a diethylene glycol, and a polyethylene glycol -- glycol ether system solvents (for example, ethylene glycol wood ether --), such as a glycerol Ethylene glycol diethylether, the diethylene-glycol monomethyl ether, Glycol ester system solvents, such as diethylene glycol monoethyl ether for example, ethylene glycol monomethyl ether acetate and ethylene glycol monoethyl ether acetate -- N-methyl pyrrolidones, such as diethylene-glycol monomethyl ether acetate, dimethyl sulfoxide, sulfolane, 1,3-dimethyl-2-imidazolidinone, etc. are mentioned. Especially 1,3-dimethyl-2-imidazolidinone is excellent also in the solubility of a fluorescence compound and binder resin, and especially desirable. A high-boiling point organic solvent can be used combining one sort or several sorts. In addition, as for the amount of the high-boiling point organic solvent used, in the case of the ink of a continuous method, it is desirable to consider as 20 or less % of the weight to all solvents.

[0034] Moreover, although the halogenide of an ionizable inorganic or organic salt, for example, alkali metal, alkaline earth metal, or the 4th class ammonium, a sulfonate, a nitrate, propionate and formate, or a thiocyanate can be added as a conductive grant agent when applying the ink constituent of this invention to ink jet printing of a continuous method, it is desirable by adjusting the addition of benzenesulfonic acid and tertiary amine in the ink constituent of this invention to adjust specific resistance.

[0035]

[Example] Below, an example explains this invention further at details. The section expresses the weight section among an example and % expresses weight %.

Raw materials other than an example 1 fluorescence compound were mixed at a following rate, and at 50 degrees C, it stirred for 50 minutes and dissolved. Added the aforementioned instantiation (compound C) 1.0 section as a fluorescence compound after cooling, and continue stirring for 5 more minutes, and it was made to dissolve, and filtered with the 0.45-micrometer membrane filter, and ink was prepared.

Polyvinyl pyrrolidone [the Tokyo Chemicals reagent and K30] The 4.3 sections P-toluenesulfonic acid The 1.3 sections Tree n butylamine The 1.7 sections Ethanol The 87.3 sections 1,3-dimethyl-2-imidazolidinone The ink of 5.0 **** is used for the ink jet printer of a continuous method. It printed to the regular paper. In viewing under a fluorescent light, although the difference with the portion which is not printed could not be found out, the printing portion emitted light in the red lamp color by the exposure of ultraviolet rays, it could read clearly, and the good printing property was shown. This ink was put at 60 degrees C for 100 hours, and the stability test in an acceleration condition was carried out. The fluorescence spectrum before and behind a trial was measured using the spectrophotofluorometer (the Shimadzu make, RF-5000). After the trial is held 90% and the fluorescence intensity in the luminescence maximum (614nm) showed good stability.

[0036] The mixed rate of raw materials other than an example 2 fluorescence compound was changed as follows, and the ink constituent was prepared, using the instantiation (compound C) 1.0 section as a fluorescence compound.

P-toluenesulfonic acid The 1.0 sections Tree n butylamine The 1.7 sections Polyvinyl butyral (Aldrich reagent) The 2.0 sections Ethanol The 89.7 sections Diethylene glycol monoethyl ether The ink of 5.0 **** is used for the ink jet printer of a continuous method. It printed to the regular paper. In viewing under a fluorescent light, although the difference with the portion which is not printed could not be found out, the printing portion emitted light in the red lamp color by the exposure of ultraviolet rays, it could read clearly, and the good printing property was shown. This ink was put at 60 degrees C for 100 hours, and the stability test in an acceleration condition was carried out. The fluorescence spectrum before and behind a trial was measured using the spectrophotofluorometer (the Shimadzu make, RF-5000). After the trial is held 91% and the fluorescence intensity in the luminescence maximum (614nm) showed good stability.

[0037] The mixed rate of raw materials other than an example 3 fluorescence compound was changed as follows, and the ink constituent was prepared, using the instantiation (compound C) 1.0 section as a fluorescence compound.

P-toluenesulfonic acid The 1.0 sections Tree n butylamine The 1.3 sections Ethyl cellulose (Wako Pure Chem reagent 10cP) The 1.3 sections Ethanol The 90.3 sections Diethylene glycol monoethyl ether The ink of 5.0 **** is used for the ink jet printer of a continuous method. It printed to the regular paper. In viewing under a fluorescent light, although the difference with the portion which is not printed could not be found out, the printing portion emitted light in the red lamp color by the exposure of ultraviolet rays, it could read clearly, and the good printing property was shown. This ink was put at 60 degrees C for 100 hours, and the stability test in an acceleration condition was carried out. The fluorescence spectrum before and behind a trial was measured using the spectrophotofluorometer (the Shimadzu make, RF-5000). After the trial is held 92% and the fluorescence intensity in the luminescence maximum (614nm) showed good stability. [0038] The mixed rate of raw materials other than an example 4 fluorescence compound was changed as follows, and the ink constituent was prepared, using the instantiation (compound B) 0.3 section as a fluorescence compound.

P-toluenesulfonic acid The 1.0 sections Tree n butylamine The 1.7 sections N-methyl pyrrolidone The 12.0 sections Ethyl acetate The 5.0 sections Methyl ethyl ketone The ink of 80.0 **** is used for the ink jet printer of a continuous method. It printed to the regular paper. In viewing under a fluorescent light, although the difference with the portion which is not printed could not be found out, the printing portion emitted light in the red lamp color by the exposure of ultraviolet rays, it could read clearly, and the good printing property was shown. This ink was put at 60 degrees C for 100 hours, and the stability test in an acceleration condition was carried out. The fluorescence spectrum before and behind a trial was measured using the spectrophotofluorometer (the Shimadzu make, RF-5000). After the trial is held 89% and the fluorescence intensity in the luminescence maximum (614nm) showed good stability.

[0039] The mixed rate of raw materials other than an example 5 fluorescence compound was changed as follows, and the ink constituent was prepared, using the instantiation (compound E) 1.0 section as a fluorescence compound.

2-naphthalene sulfonic acid The 1.3 sections Triethanolamine The 1.7 sections Vinyl chloride vinyl acetate copolymer (Aldrich reagent) The 1.0 sections 1,3-dimethyl-2-imidazolidinone The 10.0 sections Ethyl acetate The 80.0 sections Isopropanol The ink of 5.0 **** is used for the ink jet printer of a continuous method. It printed to the regular paper. In viewing under a fluorescent light, although the difference with the portion which is not printed could not be found out, the printing portion emitted light in the red lamp color by the exposure of ultraviolet rays, it could read clearly, and the good printing property was shown. This ink was put at 60 degrees C for 100 hours, and the stability test in an acceleration condition was carried out. The

fluorescence spectrum before and behind a trial was measured using the spectrophotofluorometer (the Shimadzu make, RF-5000). After the trial is held 87% and the fluorescence intensity in the luminescence maximum (614nm) showed good stability.
[0040] The mixed rate of raw materials other than an example 6 fluorescence compound was changed as follows, and the ink constituent was prepared, using the instantiation (compound A) 1.0 section as a fluorescence compound.

Benzenesulfonic acid The 1.0 sections Dimethylethanolamine The 1.5 sections Diethylene-glycol monobutyl ether The 6.5 sections Dimethyl sulfoxide The 15.0 sections N-methyl pyrrolidone The ink of 75.0 **** is used for the ink jet printer of a piezo-electric element method. It printed to the regular paper. In viewing under a fluorescent light, although the difference with the portion which is not printed could not be found out, the printing portion emitted light in the red lamp color by the exposure of ultraviolet rays, it could read clearly, and the good printing property was shown. This ink was put at 60 degrees C for 100 hours, and the stability test in an acceleration condition was carried out. The fluorescence spectrum before and behind a trial was measured using the spectrophotofluorometer (the Shimadzu make, RF-5000). After the trial is held 88% and the fluorescence intensity in the luminescence maximum (614nm) showed good stability.

[0041] The mixed rate of raw materials other than an example 7 fluorescence compound was changed as follows, and the ink constituent was prepared, using the instantiation (compound L) 0.1 section as a fluorescence compound.

P-toluenesulfonic acid The 0.1 sections Tree n butylamine The 0.3 sections Methacrylic acid methyl-methyl-acrylate copolymer [The Asahi Chemical Co., Ltd. make, DERUPETTO80N] The 10.0 section Ethyl acetate The 30.0 sections Methyl ethyl ketone Ink of 20.0 **** It applied to the regular paper. In viewing under a fluorescent light, although the difference with the portion which has not been applied could not be found out, the spreading portion emitted light in the red lamp color by the exposure of ultraviolet rays, it could identify clearly, and the good engine performance was shown. This ink was put at 60 degrees C for 100 hours, and the stability test in an acceleration condition was carried out. The fluorescence spectrum before and behind a trial was measured using the spectrophotofluorometer (the Shimadzu make, RF-5000). After the trial is held 89% and the fluorescence intensity in the luminescence maximum (614nm) showed good stability.

[0042] The mixed rate of raw materials other than an example 8 fluorescence compound was changed as follows, and the ink constituent was prepared, using the instantiation (compound C) 1.0 section as a fluorescence compound.

P-toluenesulfonic acid The 0.2 sections Triethanolamine The 0.8 sections Ethanol The

88.2 sections 1,3-dimethyl-2-imidazolidinone The ink of 9.8 **** was applied to the regular paper. In viewing under a fluorescent light, although the difference with the portion which has not been applied could not be found out, the spreading portion emitted light in the red lamp color by the exposure of ultraviolet rays, it could identify clearly, and the good engine performance was shown. This ink was put at 60 degrees C for 100 hours, and the stability test in an acceleration condition was carried out. The fluorescence spectrum before and behind a trial was measured using the spectrophotofluorometer (the Shimadzu make, RF-5000). After the trial is held 95% and the fluorescence intensity in the luminescence maximum (614nm) showed good stability. [0043] Ink was prepared like the example 8 except having changed the presentation of example of comparison 1 ink as follows.

Fluorescence compound [an instantiation compound (C)] The 1.0 sections Ethanol The 89.1 sections 1,3-dimethyl-2-imidazolidinone When the stability test in the same acceleration condition as 9.9 section examples 8 was carried out, the fluorescence intensity in the luminescence maximum (614nm) decreased to 70% after the trial.

[0044] Ink was prepared like the example 1 except having changed the presentation of example of comparison 2 ink as follows.

A fluorescence compound [an instantiation compound (C)] The 1.0 sections Polyvinyl pyrrolidone [the Tokyo Chemicals reagent and K30] The 4.3 sections Ethanol The 89.3 sections 1,3-dimethyl-2-imidazolidinone The 5.0 sections Lithium nitrate Stability test in the same acceleration condition as 1.0 section examples 1 When carried out, the fluorescence intensity in the luminescence maximum (614nm) decreased to 16% after the trial.

[0045]

[Effect of the Invention] It is an ink constituent with the fluorescence intensity large [the ink constituent of this invention] and which is colorlessness in the usual light and emits light in red by the exposure of ultraviolet rays, and the conservation stability of ink good [a constituent].